A LIQUID HYDROCARBON FUEL CELL BATTERY

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Introduction

Several types of fuel cell systems are currently under study to meet the wide range of anticipated power, weight and duty cycle requirements. However, commercial (non-military) fuel cell power systems will ultimately have to consume the more economical hydrocarbon fuels in order to compete with existing power systems. This can be accomplished in a number of ways. The hydrocarbon fuel can be fed directly to the fuel cell or it can be converted by reforming or partial oxidation to hydrogen for subsequent electrochemical oxidation. Direct hydrocarbon-air systems are generally simpler but they require acidic carbon dioxide rejecting electrolytes, thus necessitating acid resistant (noble metal) catalysts. Indirect systems can in principle use non-noble catalysts at the expense of system complexity, and in the case of the reformer-air system an expensive palladium diffusor is required.

The development of a direct liquid hydrocarbon-air fuel cell battery is being actively pursued in our laboratory. Liquid hydrocarbon fuels are particularly suitable because they are inexpensive, readily available materials with no transportation or handling problems. Furthermore, operation with liquid fuels results in a simplified carbon dioxide separation problem with no heat duty for hydrocarbon vaporization. Unfortunately, the electrochemical reactivity is inherently lower for liquid hydrocarbons relative to that of propane[1] or butane[2][3]. As a result, highly active electrode structures are required.

The development of high performance anodes (1964-65) and active cathodes has provided a tool for the evaluation of the engineering feasibility of direct hydrocarbon-air fuel cell batteries. This is particularly important since these active anodes all exhibit fuel transport into the interelectrode space. Fuel transport and carbon dioxide rejection in the interelectrode space could dictate system design and operation criteria.

Consequently, a liquid hydrocarbon (decane)-air fuel cell system was developed to assess program assumptions (interface maintaining electrodes, thermal cycling damage, 150°C operation, etc) and illustrate potential obstacles to the use of these novel electrodes in high power density batteries. Liquid decane was selected as the representative fuel because it is typical of a commercial saturated hydrocarbon fuel. Major emphasis was placed on examining the electrolyte space, flow and venting required to prevent decane transport to the cathode. This fuel transport presents a potential explosion hazard and can result in cathode poisoning. In addition, a fuel recovery scheme is required to maintain coulombic efficiency. The five cell assembly to be discussed was intended as a research tool. Therefore, no attempt was made to size or package the system into a compact low weight assembly. Rather ease of control and modification were the key consideration.

Influence of Electrode Structure on Cell Design

Electrode preparation variables can have a profound affect on cell design. Aside from their obvious role in cell output, the extent to which the control and maintain the interface between reactant streams (fuel-electrolyte, electrolyte-air)

is especially important to cell design since at the temperatures (150 to 250°C) required for effective hydrocarbon oxidation auxiliary interface control materials (membranes, matrices, etc) are almost non-existent. Thus, an effective hydrocarbon or air electrode for this system must perform a dual function. It must establish and control the reactant-catalyst-electrolyte three phase contact inside the electrode while maintaining bulk separation of the reactant and electrolyte phases to prevent gross leakage.

Anode Structure

When porous sintered platinum-Teflon gas electrodes are used in liquid hydrocarbon cells their performance is quite poor, despite the fact that they give significant activity on vaporized fuel of the same carbon number. Research with liquid decane indicated that progressive fuel flooding was responsible for this poor liquid hydrocarbon performance[2]. Furthermore, it was found that this problem could be eliminated by altering the platinum-Teflon dispersion techniques and changing sintering conditions to re-establish the desired wetproofing. This is illustrated in Figure 1. Using these techniques excellent liquid hydrocarbon electrodes can be prepared. Early structures of this type gave limiting currents in excell of 140 ma/cm² with 150°C liquid decane. In addition, further performance improvements could be obtained by incorporating a porous Teflon barrier on the fuel side of the electrode. This improved performance could not be attributed to a flow restriction phenomena, since it was found to be independent of barrier thickness between 3 and 350 mils. However, it does appear to be due to a capillary effect which controls the rate of release of the liquid fuel to the active electrode surface. This effect is not fully understood. Unfortunately, these active structures show a significant amount of fuel transport through the pores of the hydrophobic electrode. This phenomena was first reported by Shropshire, et al[3] in 1965, and attributed to either internal gasification (boiling) in the hydrophobic matrix or diffusive flow (atmolysis) akin to that observed with gaseous reactants. This diffusive flow was discussed by Katan and Allen[4]. It appears that a combination of both these effects are responsible for the liquid fuel transport observed. Recent studies indicate that fuel transport rate is independent of electrode activity (for the active systems) thus suggesting that the transport rates can be reduced while still retaining good activity. However, efforts to reduce the atmolysis rate have not met with success as yet.

Tests in small (10 cm²) total cells indicated that electrode checking and cracking occurred after repeated thermal cycling of the electrode. In addition, anode barrier separation was found to reduce electrode activity by a factor of two. Both these deficiencies were corrected by laminating a 3.5 mil fuel barrier to the preformed anode structure to produce an integral electrode structure. As indicated in Figure 1, the laminated electrode gave about the same performance as the conventional separate barrier system (within fabrication repeatability) and this laminated structure was selected as the standard for the multicell assembly. Current structures attain 200 ma/cm² at 0.45 volt polarized with limiting currents of up to 300 ma/cm².

Cathode Structure

Operation in intermediate (150-250°C) temperature electrolytes imposes more stringent cathode structure requirements than normally encountered in low temperature fuel cells. Cathodes designed for this service must maintain positive interface control after repeated temperature cycling due to start-up and shut-down sequences. This is especially important in the liquid hydrocarbon-air fuel cell systems since oxygen transport into the electrolyte space cannot be tolerated in view of the significant decane transport previously discussed.

Preliminary experiments indicated that a thin porous Teflon film (10 micron pores) applied to the air side of the cathode could provide the required interface control without loss in electrode performance. However, oxygen transport was observed with a commercial porous Teflon laminated electrode structure. Consequently, tests were conducted to determine the effect of cladding pore diameter on cathode performance and oxygen transport using Teflon films with pores ranging from 5 to 100 microns. This study indicated that pore diameter is an important parameter. Optimum oxygen and air performance was obtained when ten micron pore Teflon films were laminated to the cathode, and no oxygen transport was observed at this pore diameter.

As a result of these studies, three potential cathode systems have been developed for the hydrocarbon-air total cell system. These include a (1) 50 mg Pt/cm^2 sintered platinum Teflon electrode laminated to a 3.5 mil (10 micron pore) porous Teflon film, (similar to the anode structure) (2) a 10 mg Pt/cm^2 Cyanamid AA-1 electrode bonded to a porous Teflon film and (3) a 2.5 mg Pt/cm^2 sintered carbon Teflon structure. The air performance of these potential candidate systems are summarized in Figure 2. As expected, the cathode with the highest platinum loading gave the best performance. However, a five-fold reduction in catalyst loading was obtained with the bonded Cyanamid AA-1 electrode at the expense of only 70 mv debit. The carbon cathode was rejected because of its rather poor open circuit and load reponse and its high decane sensitivity.

Maintenance of cathode integrity has found to be the key to successful total cell operation. Therefore, a series of single and multicell tests were conducted varying cathode configuration while holding the anode configuration fixed. These tests used a 10 cm^2 (1.5 inch diameter) cell to eliminate scale-up problems and minimize hydrocarbon hold-up in the event of cathode failures. Analysis of these data indicates that the initial performance of both the clad Cyanamid AA-1 electrode and the laminated sintered platinum-Teflon studies are quite comparable despite the five-fold variation in platinum content. The average cell performance obtained in these single and multicell tests are shown in Figure 3. The five assemblies tested fell essentially on a single curve with an average peak power capability of 17 mw/cm^2 on oxygen and 14 mw/cm^2 on air. However, the best three cell stack gave 21 mw/cm^2 on oxygen and 17 mw/cm^2 on air. This compares quite well with performance projections based on half cell measurements (22 and 19 mw/cm^2 on oxygen and air respectively including cell resistance loss). Thus, both these electrodes would be suitable for total cell systems. However, the Cyanamid AA-1 structure was found to be quite sensitive to decane "poisoning" which could occur in the event of system upsets. The 10 cm^2 cell was particularly sensitive to this because of inadequate venting and decane residence space. In fact, this decane sensitivity increased with decreasing platinum loading; the 2.5 mg Pt/cm^2 carbon electrode was the most sensitive and the 50 mg Pt/cm^2 laminated cathode least sensitive. Consequently, the 50 mg/cm^2 laminated cathode was selected for use in the final 4" x 4" five cell assembly to minimize performance losses resulting from control system upsets.

Liquid Decane-Air System Description

Liquid hydrocarbon (decane) transport through the cathode cannot be ignored in cell design especially when oxygen or air transport through the cathode structure is even a remote possibility. Impingement of liquid hydrocarbon on the active cathode could result in a severe performance debit and if oxygen atmolysis occurs, and detonation is possible. In addition, the combined effect of fuel transport and carbon dioxide rejection in the interelectrode space can result in excessive cell internal resistance losses if adequate residence and venting space is not provided. The liquid decane-air five cell battery was expressly designed to mitigate some of these problems even at the expense of some stack power output.

A schematic of the 4" x 4" unit cell (80 cm^2 effective area) used in this battery is shown in Figure 4. It consists of three chambers, a central electrolyte chamber ③, inserted between the fuel ② and the air ④ chambers. The cell separator ① also serves as an electrode support partition to maintain a small inter-ference fit to insure good electrical contact between the electrode and the current collector. Air is fed to the top of the cathode chamber and exhausted at the bottom, removing product water. Liquid decane is pumped in at the bottom of the fuel chamber-- it then percolates through the porous Teflon barrier to the anode where part of the fuel is consumed electrochemically and the remainder is transported into the elec-trolyte space. Phosphoric acid (14.7 M) electrolyte is also fed from entry ports at the bottom of the cell. The electrolyte level is controlled by an exit weir located well above the active electrode zone. This provides a decane residence space above the electrodes to prevent cathode contact. The electrolyte flow rate and chamber thickness were selected to sweep the transported fuel from the cell without cathode contact. The fuel and electrolyte are separated in the electrolyte tank (using over-flow weirs) and the recovered fuel is percolated through a silica gel column prior to its return to the fuel tank for re-use. This is illustrated in a simplified system flow diagram, Figure 5. In addition, both fuel and electrolyte chambers are fitted with gas vent chambers to facilitate carbon dioxide rejection. As a safety precaution a nitrogen purge is supplied to these vents when operating with oxygen at the cathode.

Figure 6 shows the individual components of the unit cell. The plastic frame sections were fabricated from a low distortion silica filled Teflon due to creep and thermal stress problems encountered with unfilled Teflon in small cell tests. The individual cell frames serve to form the various inlet, vent and ex-haust manifolds for all the reactant streams. The electrolyte chamber thickness was set at 110 mils to insure that the 3 cm^3/min/cell electrolyte flow could sweep the transported decane into the decane residence space before it contacted the cathode. The decane residence-vent space and exit weir (shown in the back view of the elec-trolyte chamber) was also provided to help control the decane inventory. The result-ing unit cell requires 0.45 inches. However, a 0.25 inch cell could be developed for use in high power systems. The assembled five cell battery illustrated in Figure 7 is series connected using external current collection bus bars on both sides of the collector to reduce "bus bar" resistance losses in the cell current collector. This series arrangement minimizes the effect of short time voltage oscillations encountered with liquid hydrocarbon fuels at high current densities. These oscillations can be quite large (up to 0.4 volts/cell) depending on electrode structure, start-up history and current density. The overall dimensions of the stack are 6-1/4" x 6-3/4" x 4-1/2" including end plates and Belville spring closure (five cells require only 2-1/4 inches) required as a result of differential expansion on start-up and shut-down. Older closures failed to maintain stack integrity for more than one start-up shut-down cycle.

Fuel Cell System Evaluation

The liquid decane-air fuel cell battery described in the preceding section was used to determine if there is any engineering obstacle to the development of a direct liquid decane-air fuel cell battery. Towards this end, tests were conducted to study the effects of system scale-up on cell operation and electrode life. Three individual assemblies were prepared, two were used in our laboratory for systems studies, while the third was delivered to U.S.A. Electronics Command (Fort Monmouth) as a battery demonstrator.

The initial performance obtained with assemblies 1 and 3 are summarized in Figure 8. Average values were used since only three assemblies were prepared and fabricated repeatability could not be established. The oxygen performance was in fairly good agreement with the results obtained in the 1.5 inch diameter cell,

although a 200 mv (40 mv/cell) debit was observed at 5 amps. A similar response was noted on air, however, 3.5 amps was the maximum current possible without dropping below 0.2 volts/cell (a safety cut-off point). This poor air performance is probably due to some decane transport across the electrolyte chamber to the cathode since in the initial tests (Assembly 1) the performance of the individual cells proved to be sensitive to electrolyte flow distribution. This was subsequently corrected by opening an electrolyte balance pressure line to both end plate electrolyte distribution manifolds. Despite this loss the second (#3) five cell assembly produced 6 watts on oxygen and 3.5 to 3.7 watts on air.

Next the use of wide boiling range fuels was briefly examined to assess problems introduced by a realistic fuel. A special low sulfur isoparaffinic turbo-fuel (OTF-90, boiling range 195-290°C) was silica gel percolated and fed to the cell through the normal fuel feed system. The results shown in Figure 9 indicate a three-fold reduction in power capability with this isoparafinic fuel. Inspection of the operating system indicated that this was due to increased fuel transport through the anode with a resultant increased cathode debit. Indeed, significant quantities of fuel were recovered from the exit air stream. However, no performance loss was noted upon returning to the n-decane fuel. Therefore, it appears that a reduction in fuel transport should also improve performance on wide boiling range isoparaffinic fuels.

The decane-air performance history of assembly 3 is summarized in Figure 10, which is a plot of stack power (at 1-1.5 amps) versus time at 150°C (~40% of this under load). Notice that stack power drops markedly during the first 100 hours and then tends to stabilize at about 50% of its original value. As indicated in the figure, the battery was shut down three times during this program to assess the affect of thermal expansion damage on cathode performance. After the second shutdown, cathode leakage was noted which became worse after the 400 hour shut down. Thus, it appears that hydrocarbon-air batteries will have to remain at their operating temperature during their service life.

At 400 hours, some petroleum derived decane (containing alkyl aromatics) was inadvertently fed to the stack. Operation on this contaminated fuel resulted in an immediate performance loss which was not fully recovered at 560 hours when the test was terminated. This is in direct contrast to the reversible response observed with the OTF-90 fuel. A further indication that the poor performance of the wide boiling range fuel was not due to anode poisoning. From the foregoing, it appears that operation with commercial fuels is not a significant problem per se. However, some fuel purification will be required to remove sulfur, surfactants, and alkyl aromatics.

Conclusions

The development of this five cell direct liquid decane-air battery has demonstrated that operation with fuel transport is feasible. However, decane transport to the cathode can impair cell performance if the electrolyte chamber does not contain adequate decane residence and vent space. In addition, a fuel recovery system is required to maintain coulombic efficiency. Despite these problems, the five cell stack was capable of delivering 6 watts on decane-oxygen and 3.7 watts on decane air feeds. However, improved electrode structures are required since significant performance losses were noted in extended tests. These can amount to up to 50% of the initial performance especially if numerous cold shut downs are required.

Tests with a wide boiling commercial fuel (OTF-90) indicates that these fuels would present no new engineering problems, but performance is impaired due to increased fuel transport which results in an increased cathode debit. In addition, some fuel purification will be required to remove potential catalyst poisons; this problem is currently under study.

Thus, this study has established that there do not appear to be any engineering obstacles to the development of a high power density driect liquid hydro-carbon-air fuel cell battery. Unfortunately, only platinum electrodes have shown suitable electrochemical activity and the quantities required preclude any extensive commercial applications. Thus, a direct liquid hydrocarbon-air fuel cell battery is feasible provided that the noble metal catalyst requirements can be substantially re-duced through improved utilization or replacement with non-noble systems. Work in both these areas appears quite promising and ten-fold improvements in platinum utiliza-tion have already been demonstrated with experimental electrodes indicating that further improvements may be possible.

Acknowledgment

References

(1) W. T. Grubb and C. J. Michalski, Proc. 18th Annual Power Sources Conference, Atlantic City, New Jersey (May, 1964).

(2) W. R. Epperly, Proc. 19th Annual Power Sources Conference, Atlantic City, New Jersey (May, 1965).

(3) J. A. Shropshire, E. H. Okrent and H. H. Horowitz, Hydrocarbon Fuel Cell Technology (B. Baker, ed.) Academic Press, 1965, p. 539.

(4) T. Katan and G. W. Allen, To be published.

Figure 1

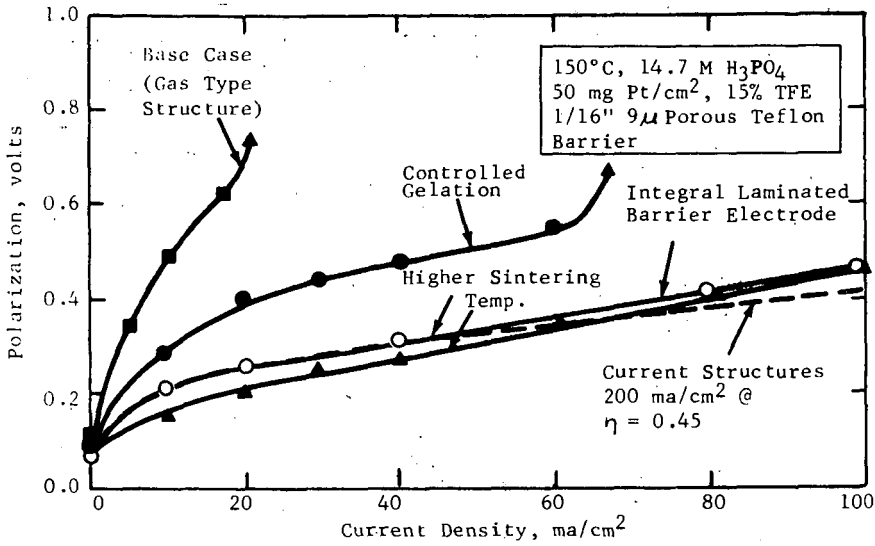Electrode Fabrication Procedure Critical
to Liquid Hydrocarbon Performance

Figure 2

Air Performance of Candidate
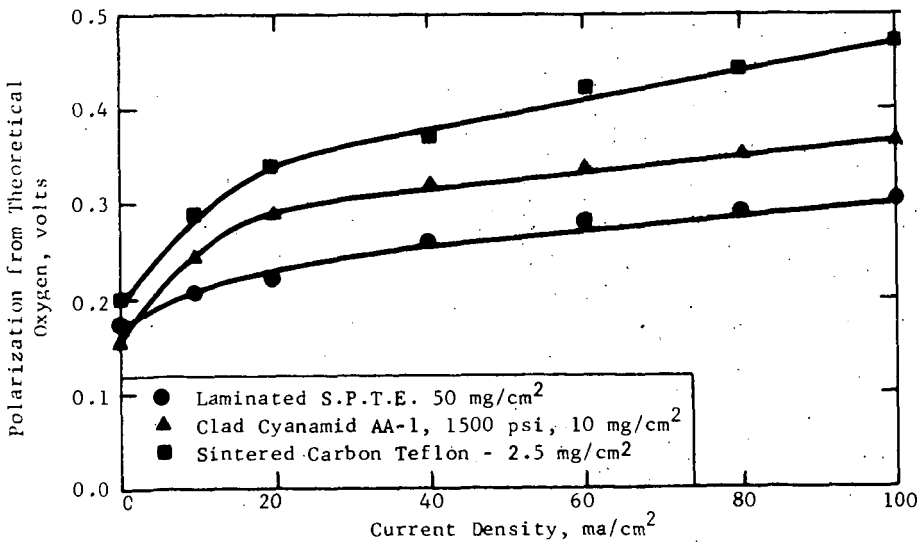Cathodes for Hydrocarbon-Air Cell

Figure 3

Initial Performance Data Decane Fuel Cells
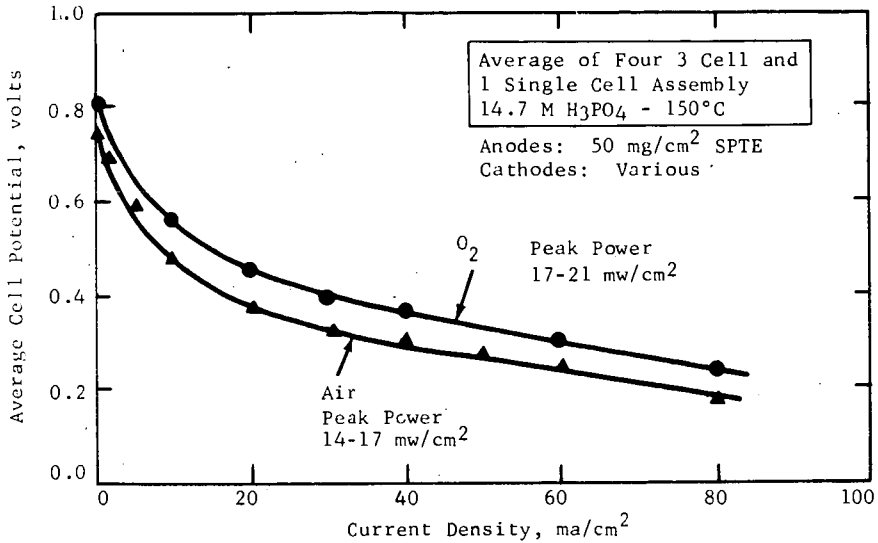
(10 cm^2 Cells)

Average of Four 3 Cell and
1 Single Cell Assembly
14.7 M H_3PO_4 - 150°C

Anodes: 50 mg/cm^2 SPTE
Cathodes: Various

O_2 Peak Power
17-21 mw/cm^2

Air
Peak Power
14-17 mw/cm^2

Average Cell Potential, volts

Current Density, ma/cm^2

Figure 4

Diagram of Individual Cell Unit

Fuel Vent
(CO_2)

Fuel Exit
Anode Barrier

Anode

Fuel Inlet

N_2

Electrolyte Vent (CO_2)
Electrolyte Exit
Air Inlet

Cathode Barrier
Cathode

Excess Air + H_2O

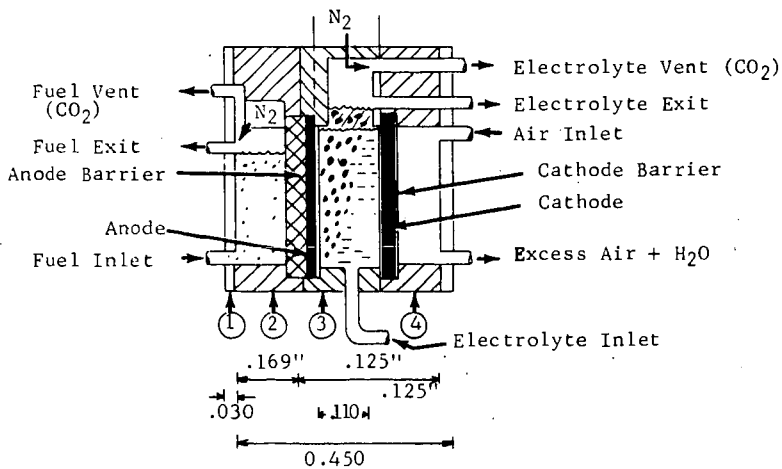Electrolyte Inlet
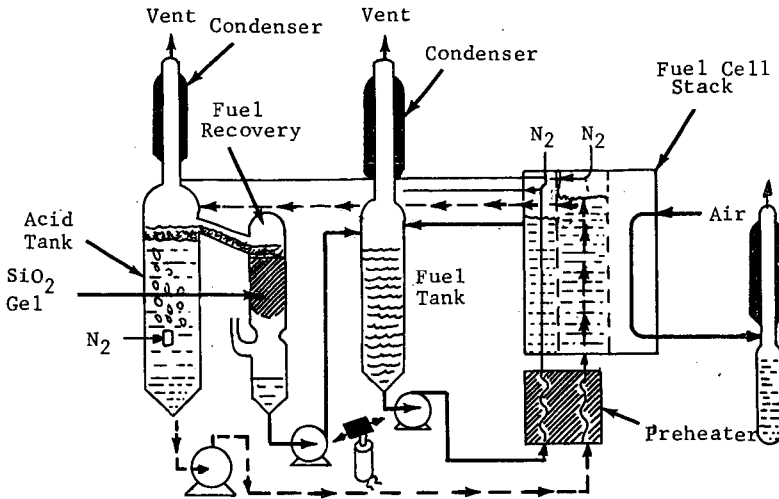
.169"   .125"
.125"
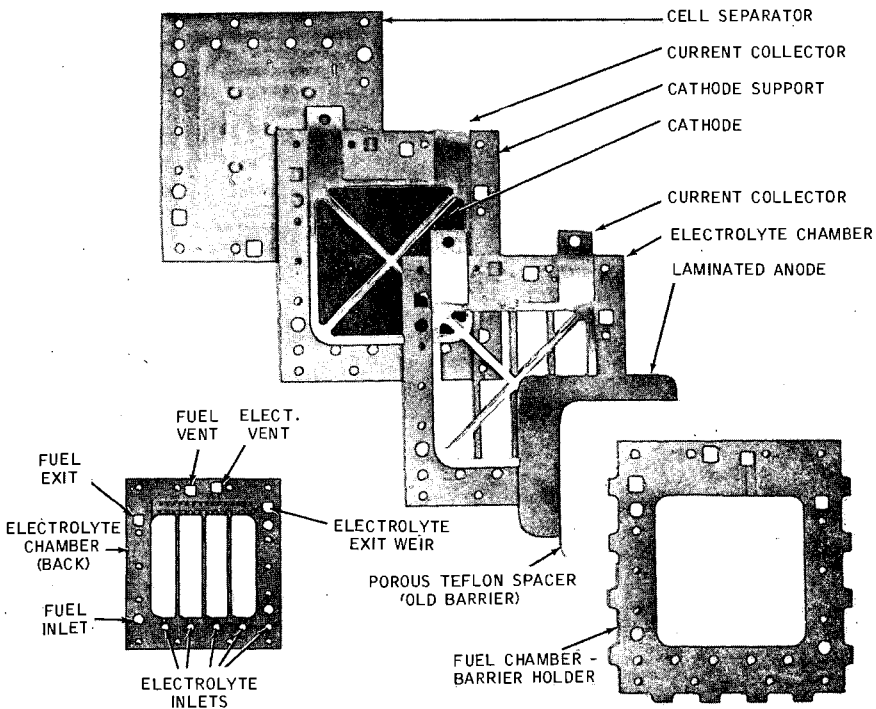.030   .110
0.450

Figure 5

Simplified Decane Air Fuel Cell Battery Schematic

Figure 6
COMPONENTS OF DECANE-AIR UNIT CELL
(SILICA FILLED TFE)
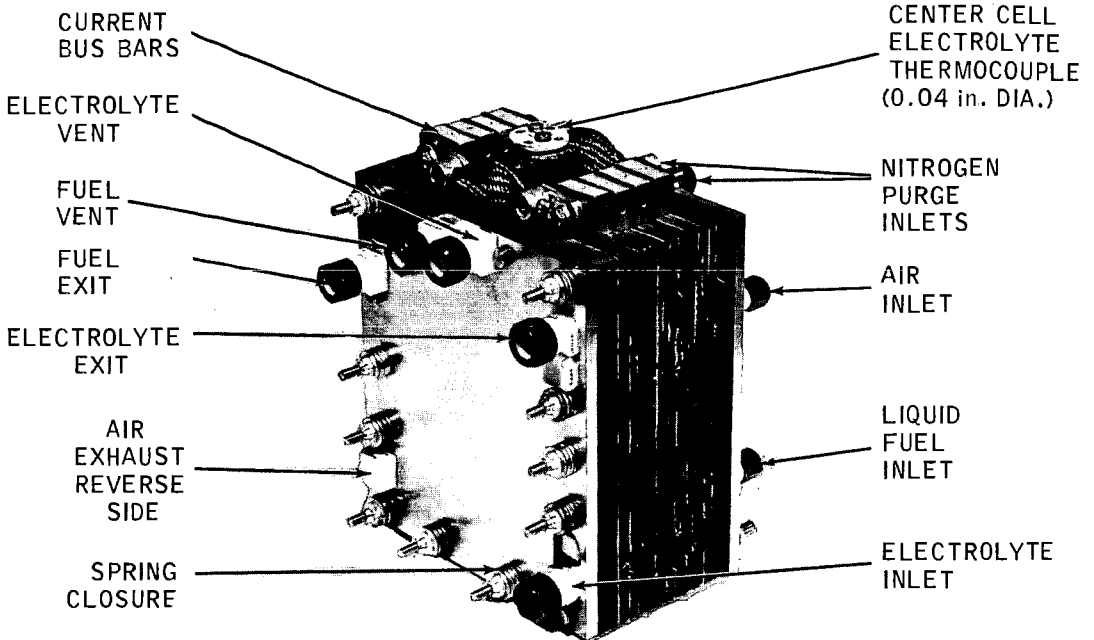
Figure 7

LIQUID DECANE-AIR FUEL CELL
FIVE CELL BATTERY

CURRENT BUS BARS

CENTER CELL ELECTROLYTE THERMOCOUPLE (0.04 in. DIA.)

ELECTROLYTE VENT

FUEL VENT

FUEL EXIT

ELECTROLYTE EXIT

AIR EXHAUST REVERSE SIDE

SPRING CLOSURE

NITROGEN PURGE INLETS

AIR INLET

LIQUID FUEL INLET

ELECTROLYTE INLET

Figure 8

Initial Performance 4" x 4" Decane Fuel Cell Assembly

(Average of Assemblies 1 and 3)

Anodes: Laminated SPTE (50 mg/cm^2)
Cathodes: Laminated SPTE (50 mg/cm^2) or Clad Cyanamid AA-1
——Predicted from 1.5 inch Diameter Total Cells

Oxygen

Air

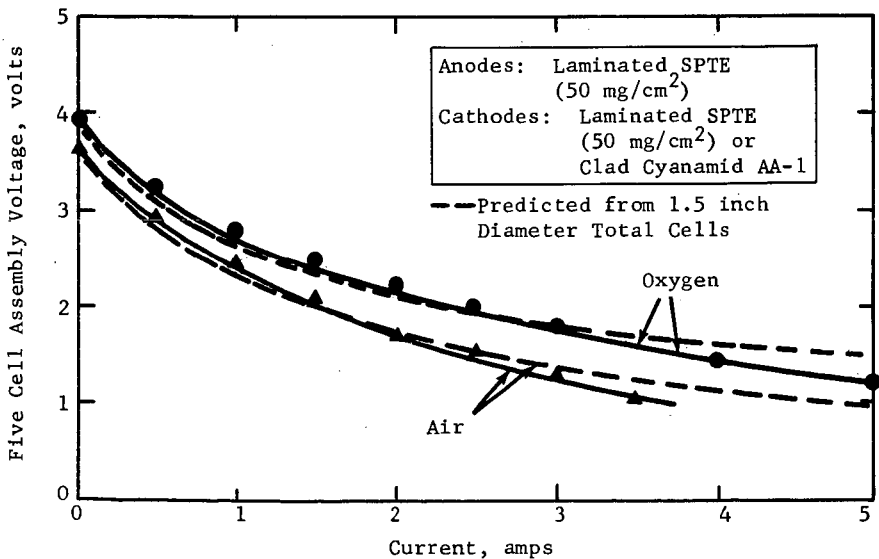Five Cell Assembly Voltage, volts
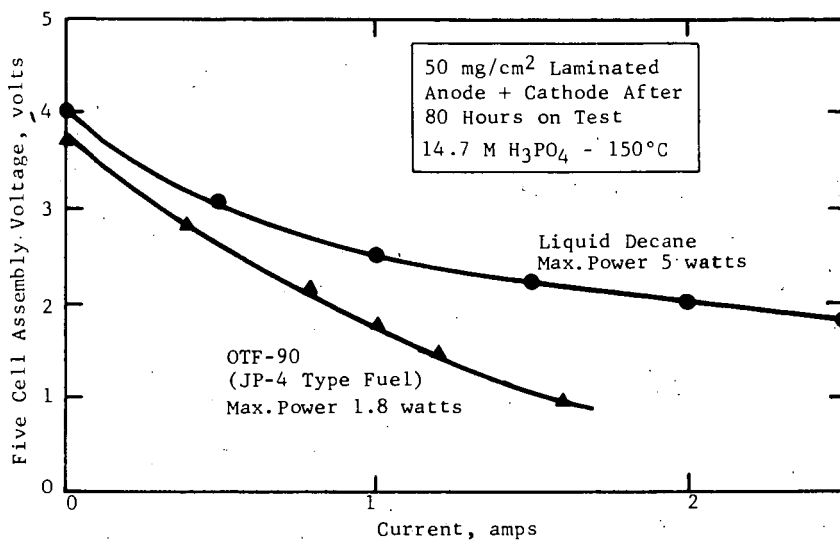
Current, amps

Figure 9

Effect of Wide Boiling Range Fuel

Figure 10

Life Test of Five Cell Decane-Air
Battery Indicates Performance Losses